

What is claimed is:

1. A composition for use in forming a porcelain enamel coating having a metallic appearance, said composition including a glass component comprising a glass frit, said glass frit comprising by weight: about 45% to about 55%  $\text{SiO}_2$ , about 4 to about 20%  $\text{R}_2\text{O}$ , about 9 to about 15%  $\text{B}_2\text{O}_3$ , about 4 to about 12%  $\text{MnO}_2$ , about 1.5 to about 7%  $\text{F}_2$ , about 0% to about 20%  $\text{MO}_2$ , about 0% to about 10%  $\text{RO}$ , about 0% to about 6%  $\text{NO}_2$ , about 0% to about 2%  $\text{P}_2\text{O}_5$ , about 0% to about 3%  $\text{CoO}$ , about 0% to about 3%  $\text{NiO}$ , about 0% to about 3%  $\text{Al}_2\text{O}_3$ , about 0% to about 3%  $\text{Fe}_2\text{O}_3$ , about 0% to about 3%  $\text{CuO}$ , about 0% to about 4%  $\text{ZrO}_2$ , about 0% to about 2%  $\text{Nb}_2\text{O}_5$ , and about 0% to about 5%  $\text{Sb}_2\text{O}_3$ , wherein  $\text{R}_2\text{O}$  represents at least one alkali oxide, wherein  $\text{RO}$  represents at least one alkaline earth oxide and wherein  $\text{M}$  represents at least one transition metal.
2. The composition of claim 1, wherein  $\text{R}_2\text{O}$  is selected from the group consisting of  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$  and  $\text{K}_2\text{O}$ , or combinations thereof.
3. The composition of claim 1 wherein  $\text{MO}_2$  is selected from the group consisting of  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{TiO}_2$  and  $\text{CeO}_2$ .
4. The composition of claim 1 wherein  $\text{RO}$  is selected from the group consisting of  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ , and  $\text{BaO}$ .
5. The composition of claim 1 further comprising an oxide pigment, selected from the group consisting of iron brown hematite; cobalt silicate blue olivine; nickel barium titanium primrose priderite; lead antimonite yellow pyrochlore; nickel antimony titanium yellow rutile; nickel niobium titanium yellow rutile; nickel tungsten yellow rutile; chrome antimony titanium buff; chrome niobium titanium buff rutile; chrome tungsten titanium buff rutile; manganese antimony titanium

buff rutile; titanium vanadium antimony grey rutile; manganese chrome antimony titanium brown rutile; manganese niobium titanium brown rutile; cobalt aluminate blue spinel; zinc chrome cobalt aluminum spinel; cobalt chromate blue-green spinel; cobalt titanate green spinel; iron chromite brown spinel; iron titanium brown spinel; nickel ferrite brown spinel; zinc ferrite brown spinel; zinc iron chromite brown spinel; copper chromite black spinel; iron cobalt chromite black spinel; chrome iron manganese brown spinel; chrome iron nickel black spinel; chrome manganese zinc brown spinel; nickel manganese iron chromium black; tin vanadium yellow cassiterite; chrome tin orchid cassiterite; chrome tin pink sphene, and combinations thereof.

6. The composition of claim 1 further comprising a crystalline component wherein the crystalline component comprises additives selected from the group consisting of  $\text{TiO}_2$ ,  $\text{ZrSiO}_4$ ,  $\text{Zn}_2\text{SiO}_4$ ,  $\text{Bi}_{12}\text{SiO}_{20}$ ,  $\text{Bi}_4(\text{SiO}_4)_3$ , and  $\text{Bi}_2\text{SiO}_5$ ,  $2\text{ZnO} \bullet 3\text{TiO}_2$ ,  $\text{Bi}_2\text{O}_3 \bullet \text{SiO}_2$ ,  $\text{Bi}_2\text{O}_3 \bullet 2\text{TiO}_2$ ,  $2\text{Bi}_2\text{O}_3 \bullet 3\text{TiO}_2$ ,  $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{Bi}_2\text{Ti}_2\text{O}_7$ ,  $\text{Bi}_{12}\text{TiO}_{20}$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , and  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ .
7. The composition of claim 1 further comprising a mill addition selected from the group consisting of mica particles; clays; urea; boric acid, molybdic acid; sodium molybdate; copper chloride, and the chlorides, carbonates, and hydroxides, of sodium, potassium, magnesium, and calcium, and combinations thereof.
8. The composition of claim 1 further comprising a titanium opacified frit wherein the titanium opacified frit comprises by weight:  $\text{SiO}_2$  (33-57%),  $\text{B}_2\text{O}_3$  (0-23%),  $\text{TiO}_2$  (13-26%),  $\text{F}_2$  (0-9%),  $\text{NO}_2$  (1-10%),  $\text{Na}_2\text{O}$  (5-20%),  $\text{K}_2\text{O}$  (0-13%),  $\text{Li}_2\text{O}$  (0-4%),  $\text{Al}_2\text{O}_3$  (0-6%),  $\text{AuO}$  (0-0.05%),  $\text{BaO}$  (0-5%),  $\text{CaO}$  (0-2.5%),  $\text{CoO}$  (0-0.05%),  $\text{MgO}$  (0-1.5%),  $\text{P}_2\text{O}_5$  (0-4%),  $\text{Sb}_2\text{O}_3$  (0-1.5%),  $\text{ZnO}$  (0-23%), and  $\text{ZrO}_2$  (0-10%).

9. The composition of claim 8, wherein  $R_2O$  is selected from the group consisting of  $Na_2O$ ,  $Li_2O$  and  $K_2O$ , and combinations thereof.
10. The composition of claim 8 wherein  $MO_2$  is selected from the group consisting of  $ZrO_2$ ,  $SnO_2$ ,  $TiO_2$ , and  $CeO_2$ .
11. The composition of claim 8 wherein  $RO$  is selected from the group consisting of  $MgO$ ,  $CaO$ ,  $SrO$ , and  $BaO$ .
12. The composition of claim 8 further comprising an oxide pigment, selected from the group consisting of iron brown hematite; cobalt silicate blue olivine; nickel barium titanium primrose priderite; lead antimonite yellow pyrochlore; nickel antimony titanium yellow rutile; nickel niobium titanium yellow rutile; nickel tungsten yellow rutile; chrome antimony titanium buff; chrome niobium titanium buff rutile; chrome tungsten titanium buff rutile; manganese antimony titanium buff rutile; titanium vanadium antimony grey rutile; manganese chrome antimony titanium brown rutile; manganese niobium titanium brown rutile; cobalt aluminate blue spinel; zinc chrome cobalt aluminum spinel; cobalt chromate blue-green spinel; cobalt titanate green spinel; iron chromite brown spinel; iron titanium brown spinel; nickel ferrite brown spinel; zinc ferrite brown spinel; zinc iron chromite brown spinel; copper chromite black spinel; iron cobalt chromite black spinel; chrome iron manganese brown spinel; chrome iron nickel black spinel; chrome manganese zinc brown spinel; nickel manganese iron chromium black; tin vanadium yellow cassiterite; chrome tin orchid cassiterite; chrome tin pink sphene, and combinations thereof.
13. The composition of claim 1 further comprising a luster frit, wherein the luster frit comprises by weight:  $SiO_2$  (46-54%),  $B_2O_3$  (15-17%),  $MnO_2$  (8-10%),  $F_2$  (1.7-

3.5%), Na<sub>2</sub>O (5-20%), K<sub>2</sub>O (2-9%), NO<sub>2</sub> (0-6%), Li<sub>2</sub>O (0-4%), Al<sub>2</sub>O<sub>3</sub> (0-2%), BaO (0-5%), CaO (0-1%), CoO (0-1%), CuO (0-1%), Fe<sub>2</sub>O<sub>3</sub> (0-2%), NiO (0-1%), P<sub>2</sub>O<sub>5</sub> (0-3%), and Sb<sub>2</sub>O<sub>3</sub> (0-3%).

14. The composition of claim 1 further comprising a clear/semi-opaque frit, wherein the clear/semi-opaque frit comprises: SiO<sub>2</sub> (46-57%), B<sub>2</sub>O<sub>3</sub> (11-17%), Na<sub>2</sub>O (5-20%), F<sub>2</sub> (1-10%), TiO<sub>2</sub> (0-13%), NO<sub>2</sub> (0-4%), K<sub>2</sub>O (0-12%), Li<sub>2</sub>O (0-4%), Al<sub>2</sub>O<sub>3</sub> (0-3%), BaO (0-5%), CaO (0-3%), MgO (0-1%), P<sub>2</sub>O<sub>5</sub> (0-2%), ZnO (0-3%), and ZrO<sub>2</sub> (0-3%).
15. A composition for use in forming a porcelain enamel coating having a metallic appearance, comprising:
  - a. an amount (A) of a glass component comprising a metallic appearance frit;
  - b. an amount (B) of a second frit selected from the group consisting of luster frits or clear/semi-opaque frits;
  - c. wherein the weight ratio of A to B is about 1:1 to about 9:1, and
  - d. wherein the metallic appearance frit comprises SiO<sub>2</sub> (45-55%), R<sub>2</sub>O (4-20%), B<sub>2</sub>O<sub>3</sub> (9-15%), MnO<sub>2</sub> (4-12%), F<sub>2</sub> (1.5-7%), MO<sub>2</sub> (0-20%), RO (0-10%), NO<sub>2</sub> (0-6%), P<sub>2</sub>O<sub>5</sub> (0-2%), CoO (0-3%), NiO (0-3%), Al<sub>2</sub>O<sub>3</sub> (0-3%), Fe<sub>2</sub>O<sub>3</sub> (0-3%), CuO (0-3%), ZrO<sub>2</sub> (0-4%), Nb<sub>2</sub>O<sub>5</sub> (0-2%), and Sb<sub>2</sub>O<sub>3</sub> (0-5%),
  - e. wherein M represents a transition metal; wherein R<sub>2</sub>O represents one or more alkali oxides, and wherein RO represents one or more alkaline earth oxides.

16. The composition of claim 15 wherein  $\text{MO}_2$  is present in an amount not exceeding about 20 wt%, and wherein  $\text{MO}_2$  is selected from the group consisting of  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ , and  $\text{La}_2\text{O}_3$ .
17. The composition of claim 15 wherein the second frit comprises a luster frit, wherein the luster frit comprises:  $\text{SiO}_2$  (46-54%),  $\text{B}_2\text{O}_3$  (15-17%),  $\text{F}_2$  (1.7-3.5%),  $\text{Na}_2\text{O}$  (5-20%),  $\text{K}_2\text{O}$  (2-9%),  $\text{MnO}_2$  (8-10%),  $\text{NO}_2$  (0-6%),  $\text{Li}_2\text{O}$  (0-4%),  $\text{Al}_2\text{O}_3$  (0-2%),  $\text{BaO}$  (0-5%),  $\text{CaO}$  (0-1%),  $\text{CoO}$  (0-1%),  $\text{CuO}$  (0-1%),  $\text{Fe}_2\text{O}_3$  (0-2%),  $\text{NiO}$  (0-1%),  $\text{P}_2\text{O}_5$  (0-3%), and  $\text{Sb}_2\text{O}_3$  (0-3%).
18. The composition of claim 15 wherein the second frit comprises a semi-opaque frit, wherein the semi-opaque frit comprises:  $\text{SiO}_2$  (46-57%),  $\text{B}_2\text{O}_3$  (11-17%),  $\text{F}_2$  (1-10%),  $\text{Na}_2\text{O}$  (5-20%),  $\text{TiO}_2$  (0-13%),  $\text{NO}_2$  (0-4%),  $\text{K}_2\text{O}$  (0-12%),  $\text{Li}_2\text{O}$  (0-4%),  $\text{Al}_2\text{O}_3$  (0-3%),  $\text{BaO}$  (0-5%),  $\text{CaO}$  (0-3%),  $\text{MgO}$  (0-1%),  $\text{P}_2\text{O}_5$  (0-2%),  $\text{ZnO}$  (0-3%), and  $\text{ZrO}_2$  (0-3%).
19. The composition of claim 1 wherein the glass frit comprises by weight: about 45% to about 55%  $\text{SiO}_2$ , about 4 to about 20%  $\text{R}_2\text{O}$ , about 9 to about 15%  $\text{B}_2\text{O}_3$ , about 4 to about 12%  $\text{MnO}_2$ , about 1.5 to about 7%  $\text{F}_2$ , and at least one of the following oxides, not to exceed the indicated amount:  $\text{MO}_2$  (20%),  $\text{RO}$  (10%),  $\text{NO}_2$  (6%),  $\text{P}_2\text{O}_5$  (2%),  $\text{CoO}$  (3%),  $\text{NiO}$  (3%),  $\text{Al}_2\text{O}_3$  (3%),  $\text{Fe}_2\text{O}_3$  (3%),  $\text{CuO}$  (3%),  $\text{ZrO}_2$  (4%),  $\text{Nb}_2\text{O}_5$  (2%), and  $\text{Sb}_2\text{O}_3$  (5%), wherein  $\text{R}_2\text{O}$  represents at least one alkali oxide, wherein  $\text{RO}$  represents at least one alkaline earth oxide and wherein  $\text{M}$  represents at least one transition metal.
20. An appliance comprising a porcelain enamel coating having a metallic appearance, said coating formed by firing the composition of claim 1.